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FUNCTIONS FOR THE CALCULATION OF

ENTROPY, ENTHALPY, AND INTERNAL ENERGY FOR REAL FLUIDS USING EQUATIONS OF STATE AND SPECIFIC HEATS

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Abstract

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General integral equations for the determination of entropy, enthalpy, and internal energy are derived. In the first part of this paper the integration path is taken to be on the real gas surface thus yielding one set of equations. In the latter part of this paper the integration path is defined such that ideal gas specific heats and reference properties are introduced. The latter set of integral equations are applied to a particular equation of state resulting in algebraic expressions for the entropy, enthalpy, and internal energy.

FUNCTIONS FOR THE CALCULATION OF ENTROPY, ENTHALPY, AND INTERNAL ENERGY FOR REAL FLUIDS USING EQUATIONS OF STATE AND SPECIFIC HEATS

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INTRODUCTION

Several recent publications [1, 2, 3, 4, 5] from this laboratory on the calculation of thermodynamic properties of cryogenic fluids contain various relations for the determination of entropy, enthalpy, and internal energy. Considerable interest has been expressed about the derivation and application of these equations; this interest generally results from the fact that standard texts on thermodynamics are, almost without exception, inadequate in the presentation of material on the calculation of thermodynamic properties. The purpose of this paper is to derive the functions necessary for the calculation of thermodynamic properties. These derivations are intended to give the reader a better understanding of the methods of calculating thermodynamic properties and thus of the limitations of the tables so produced.

In the first part of this paper, general thermodynamic relations are presented for the calculation of thermodynamic properties from functions representing P-V-T and specific heat, velocity of sound or Joule-Thomson data. In the latter part of the paper, the equations for thermodynamic properties are developed in terms of zero-pressure, i.e., ideal gas, specific heats and are applied to a particular equation of state.

NOTATION

- P absolute pressure
- T absolute temperature
- V specific volume
- ρ density = 1/V
- S specific entropy
- H specific enthalpy
- U specific internal energy
- $\mathbf{C}_{\mathbf{p}}$ specific heat capacity at constant pressure
- C_{V} specific heat capacity at constant volume
- C_{σ} specific heat capacity at constant saturation
- W velocity of sound
- μ Joule-Thomson coefficient
- R universal gas constant

Superscripts

- o denotes an ideal gas property
- * denotes a property (real or ideal) at very low pressures ($P \approx 0$)
- " denotes a saturated vapor property
- " denotes a saturated liquid property

Subscripts

- o denotes a reference state property
- c denotes a critical point property

Subscripts on partial derivatives or integrals indicate the property to be held constant and, in addition, the subscript σ indicates constant saturation.

GENERAL THERMODYNAMIC RELATIONS AND CALCULATIONS

•Basic relations such as Maxwell's equations (1) and (2), definitions of specific heats and enthalpy (3), (4), (5), and (8) and two other thermodynamic equations, (6) and (7), are presented in many elementary thermodynamic texts.

$$\left(\frac{\partial E}{\partial P}\right)_{TP} = -\left(\frac{\partial V}{\partial T}\right)_{PP} \tag{1}$$

$$\left(\frac{\partial \Lambda}{\partial E}\right)^{LL} = \left(\frac{\partial L}{\partial E}\right)^{\Lambda} \tag{5}$$

$$C^{\Lambda} = I \left(\frac{\partial L}{\partial R} \right)^{\Lambda} = \left(\frac{\partial L}{\partial \Omega} \right)^{\Lambda}$$
 (3)

$$C_{\mathbf{p}} = T \left(\frac{\partial S}{\partial T} \right)_{\mathbf{p}} = \left(\frac{\partial H}{\partial T} \right)_{\mathbf{p}}$$
 (4)

$$C_{\sigma} = T \left(\frac{dS}{dT} \right)_{\sigma} = \left(\frac{dU}{dT} \right)_{\sigma} + P \left(\frac{dV}{dT} \right)_{\sigma}$$
 (5)

$$\left(\frac{\partial U}{\partial V}\right)_{TT} = T \left(\frac{\partial P}{\partial T}\right)_{V} - P \tag{6}$$

$$\left(\frac{\partial H}{\partial P}\right)_{T} = V - T \left(\frac{\partial V}{\partial T}\right)_{P} \tag{7}$$

$$H = U + PV \tag{8}$$

These equations illustrate that P-V-T relations are sufficient to determine entropy, enthalpy and internal energy differences along isothermal paths. In addition, it may also be observed that the

variations in S, U, and H along isobars or isometrics can be determined from the corresponding specific heats at constant pressure or volume, respectively, but not from P-V-T relations alone. Thus the changes in S, U, or H between two state points are calculated by integrating along a series of isotherms and isobars or isometrics. (Once either H or U has been determined the other may be obtained from (8).) The isothermal changes in S and U, with V as an independent variable, obtained by integrating equations (2) and (6) with respect to volume are respectively

$$\Delta S_{T} = \int_{V_{1}}^{V_{2}} \left(\frac{\partial P}{\partial T} \right)_{V} dV, \qquad (9)$$

$$\Delta U_{T} = \int_{V_{1}}^{V_{2}} \left[T \left(\frac{\partial P}{\partial T} \right)_{V} - P \right] dV.$$
 (10)

(The subscript "T" indicates the path is isothermal.)

If, instead, P is considered an independent variable, the isothermal changes in S and H obtained by integrating equations (1) and (7) with respect to pressure are respectively

$$\Delta S_{T} = \frac{1}{T} \int_{P_{1}}^{P_{2}} \left(\frac{\partial V}{\partial T} \right)_{P} dP, \qquad (9a)$$

$$\Delta H_{T} = \int_{P_{1}}^{P_{2}} \left[V - T \left(\frac{\partial V}{\partial T} \right)_{P} \right] dP.$$
 (10a)

The changes in S and H along an isobar obtained by integrating equation (4) with respect to temperature are respectively

$$\Delta S_{P} = \int_{T_{1}}^{T_{2}} \frac{C_{p}}{T} dT, \qquad (11)$$

$$\Delta H_{P} = \int_{T_{1}}^{T_{2}} C_{p} dT_{\bullet}$$
 (12)

Along isometrics, the changes in S and U obtained by integrating equation (3) with respect to temperature are respectively

$$\Delta S_{V} = \int_{T_{1}}^{T_{2}} \frac{C_{V}}{T} dT, \qquad (13)$$

$$\Delta U_{V} = \int_{T_{1}}^{T_{2}} C_{V} dT. \qquad (14)$$

It is also desirable to calculate property changes along paths of constant saturation. The changes in entropy and internal energy along saturation found by integrating equation (5) with respect to temperature are

$$\Delta S_{\sigma} = \int_{T_1}^{T_2} \frac{C_{\sigma}}{T} dT, \qquad (15)$$

$$\Delta U_{\sigma} = \int_{T_{1}}^{T_{2}} \left[C_{\sigma} - P \left(\frac{dV}{dT} \right)_{\sigma} \right] dT, \qquad (16)$$

where V and P are the saturated volume and vapor pressure, respectively, and are functions of temperature alone.

A typical integration path is illustrated in Fig. 1. The point "O" is an arbitrary reference state while the path \overline{AB} is a constant pressure path along which C_p is known. The equation of state is considered to be explicit in pressure. The application of equations (9) and (10) to the isothermal paths \overline{OA} and \overline{BC} and equations (11) and (12) to \overline{AB} results in the following relations giving S, H, and U at the point C with respect to the reference values S_O , H_O , and U_O respectively.

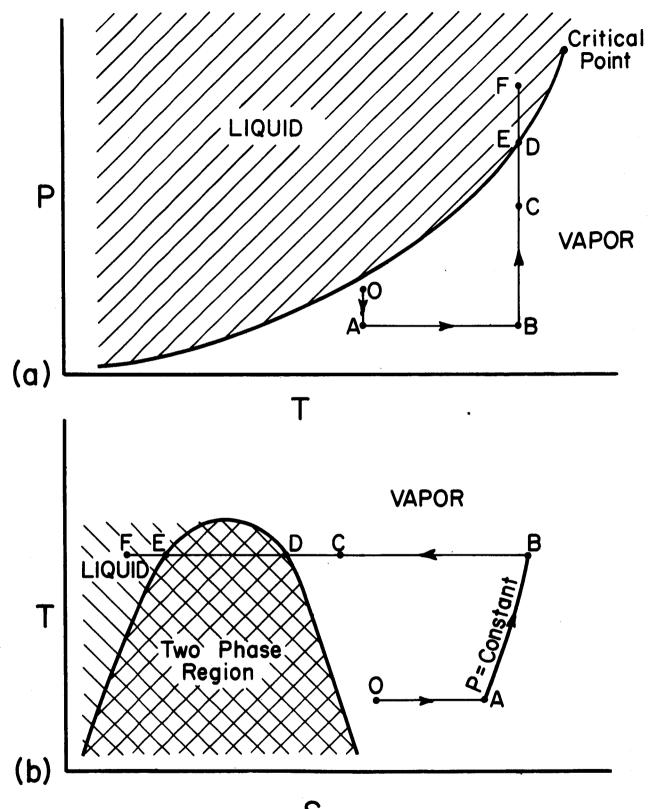


Figure 1 Typical path of integration in (a) P-T and (b) T-S coordinates

$$S = S_{o} + \int_{V_{o}}^{V_{A}} \left(\frac{\partial P}{\partial T}\right)_{V} dV + \int_{T}^{V} \left(\frac{\partial P}{\partial T}\right)_{V} dV + \int_{P_{A}}^{T} \frac{C_{p}}{T} dT, \quad (17)$$

$$H = H_{O} + \frac{L^{O}}{\sqrt{\Lambda}} \left[L \left(\frac{\partial L}{\partial D} \right)^{A} - L \right] dA + \frac{L}{\sqrt{\Lambda}} \left[L \left(\frac{\partial L}{\partial D} \right)^{A} - L \right] dA$$

+
$$\int_{P_A}^{T} C_p dT + P_A V_A - P_O V_O + PV - P_B V_B$$
, (18)

$$U = U_o + (H - H_o) - (PV - P_oV_o).$$
 (19)

It is important to note the quantities V_A and V_B in the above equations are each defined by the intersection of an isobar and an isotherm and thus the equation of state, P = P(V,T), must be solved for V. These volumes can usually be obtained by an iterative process such as the Newton-Raphson method. The necessity of solving for volume is eliminated if the path \overline{AB} is an isometric along which C_V is known. With reference to Fig. 1, it can also be seen that a point such as F in the liquid region can be reached by a path through the two phase region. This, however, requires additional data to define the two phase boundary, in particular, the variation of the vapor pressure with temperature. The changes in S, H, and U across this two phase region may then be determined from the Clapeyron relationship (20).

$$\left(\frac{\mathrm{dP}}{\mathrm{dT}}\right)_{\sigma} = \frac{\mathrm{S}^{1\eta} - \mathrm{S}^{1}}{\mathrm{V}^{11} - \mathrm{V}^{1}}$$
or
$$T(\mathrm{S}^{11} - \mathrm{S}^{1}) = \mathrm{H}^{11} - \mathrm{H}^{11} = T\left(\frac{\mathrm{dP}}{\mathrm{dT}}\right)_{\sigma} (\mathrm{V}^{11} - \mathrm{V}^{1}), \tag{20}$$

where the prime notations are used to distinguish the properties of the two phases at the same temperature and $(dP/dT)_{\sigma}$ is the slope of the vapor pressure curve.

Thus, for any point in the liquid, S, H, and U may be obtained from equations similar to (17), (18), and (19) with the addition of the appropriate value from (20). Convenient checks on the validity of the saturated liquid properties obtained in this manner may be obtained by utilizing latent heat data or by the calculation of S, H, and U along saturation from C_{σ} data with equation (15) and (16).

Other property relations may also be considered for the calculation of specific heat values from alternate thermodynamic data. These values may be used in the absence of experimental specific heat data or to check those data which are available. For example, C_p may be calculated from equation (21) with velocity of sound data, where the derivative $\left(\frac{\partial V}{\partial P}\right)_S$ is calculated from (22) which is valid for small amplitude sound propagation.

$$C_{\rm p} = \frac{\left(\frac{\partial P}{\partial V}\right)^{\rm S} - \left(\frac{\partial P}{\partial V}\right)^{\rm L}}{\left(\frac{\partial P}{\partial V}\right)^{\rm E}}$$
(21)

$$\left(\frac{\partial \mathbf{V}}{\partial \mathbf{P}}\right)_{\mathbf{S}} = -\frac{\mathbf{W}^{2}}{\mathbf{V}^{2}} \quad , \tag{22}$$

where W is the velocity of sound. It is also possible to obtain C_p values from Joule-Thomson coefficients, μ , with equation (23).

$$C_{p} = \frac{1}{\mu} \left[T \left(\frac{\partial V}{\partial T} \right)_{p} - V \right]$$
 (23)

Caution should be observed in considering the use of (21) and (23) inasmuch as the differences involved in both equations may become very small, and thus produce large relative errors in the ${\tt C}_{\tt p}$ values.

THERMODYNAMIC PROPERTY CALCULATIONS BASED ON P-V-T RELATIONS AND ZERO-PRESSURE SPECIFIC HEATS

Significant errors in thermodynamic properties calculated as previously described may arise from the uncertainty in the specific heat data. These errors may be reduced significantly by using zero-pressure specific heats calculated by the methods of statistical mechanics with spectroscopic data, since ideal gas properties are generally about an order of magnitude more accurately known than the real gas properties determined by calorimetric methods.

In extending the isotherms of the path of integration shown in Fig. 1 such that \overline{AB} approaches the zero-pressure isobar, it is clear that the representation of the P-V-T surface for the real gas must be valid to these low pressures. (The value of PV from the real gas equation of state must approach RT as P approaches zero.) As a consequence, it now also becomes convenient to choose the reference state on the ideal gas surface. Since a reference point at zero pressure would result in infinite entropies at any finite pressure on the real or ideal gas surface, the standard reference state is usually chosen at 1 atmosphere and T_0 on the ideal gas surface; this is equivalent to choosing the standard reference values of enthalpy and internal energy at zero pressure and T_0 as H^0 and U^0 are functions of temperature alone for the ideal gas.

The path of integration for the following derivation is illustrated in Fig. 2.

Equations (24) and (25) are obtained by applying (9) and (10) to the paths \overline{OA} and \overline{BC} and (11) and (12) to \overline{AB} .

$$S = S_{T_{O}}^{O} + \lim_{P \to O} \left[\int_{V_{O}}^{V_{A}} \left(\frac{\partial P}{\partial T} \right)_{V} dV + \int_{T}^{V} \left(\frac{\partial P}{\partial T} \right)_{V} dV + \int_{P^{*}}^{T} \left(\frac{c_{p}^{*}}{T} dT \right) \right]$$
(24)

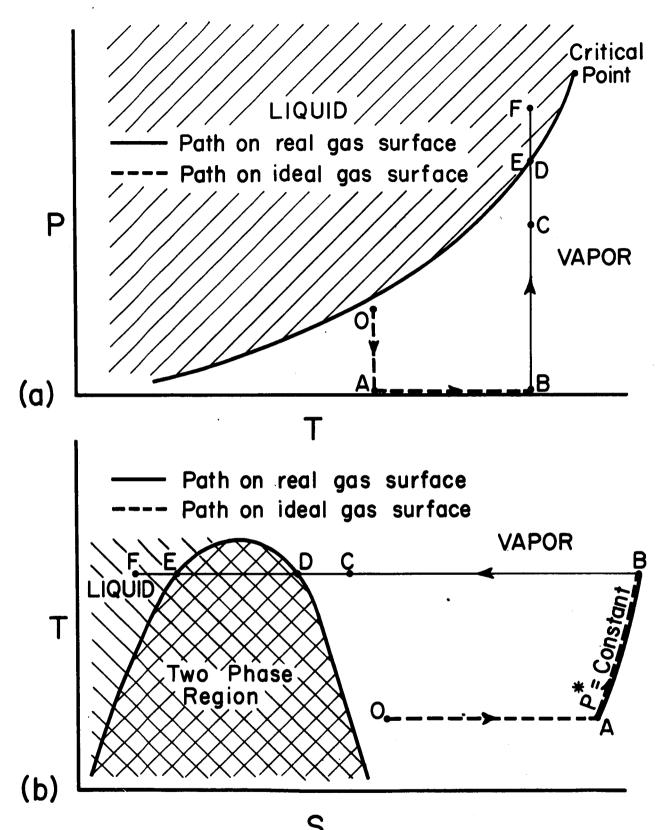


Figure 2 Path of integration from ideal to real gas surface on (a) P-T and (b) T-S coodinates

$$H = H_{T_O}^{\circ} + \lim_{P^* \to O} \left[\int_{V_O}^{V_A^*} \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV + \int_{V_B^*}^{V} \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV \right] + \int_{P^*}^{T} C_P^* dT + P^* V_A^* - P_O V_O + PV - P^* V_B^* \right].$$
(25)

It is necessary to introduce the limit as P^* approaches zero, since only then do the real and ideal surfaces coincide. Since for the ideal gas $\left(\frac{\partial P}{\partial T}\right)_V$ is independent of temperature, $\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$, the first integral in (24), can be evaluated at any temperature T.

$$\int_{\mathbf{T}_{\mathbf{Q}}}^{\mathbf{V}_{\mathbf{A}}^{*}} \left(\frac{\partial \mathbf{P}}{\partial \mathbf{T}} \right)_{\mathbf{V}} d\mathbf{V} = \int_{\mathbf{T}}^{\mathbf{V}_{\mathbf{A}}^{*}} \left(\frac{\partial \mathbf{P}}{\partial \mathbf{T}} \right)_{\mathbf{V}} d\mathbf{V}$$

This integral is then replaced by three integrals

$$\int_{V_{O}}^{V_{A}^{*}} \left(\frac{\partial P}{\partial T} \right)_{V} dV = \int_{V_{O}}^{V} \left(\frac{\partial P}{\partial T} \right)_{V} dV + \int_{T}^{V_{B}^{*}} \left(\frac{\partial P}{\partial T} \right)_{V} dV + \int_{T}^{V_{A}^{*}} \left(\frac{\partial P}{\partial T} \right)_{V} dV ,$$

and finally evaluated using $V_B^* = \frac{RT}{P^*}$ and $V_A^* = \frac{RT_O}{P^*}$ to obtain

$$\int_{V_O}^{V_A^*} \left(\frac{\partial P}{\partial T} \right)_V dV = R \ln \frac{VT_O}{V_O T} - \int_{V_B^*}^{V} \frac{R}{V} dV .$$

Substitution into equation (24) yields in the limit

$$S = S_{T_0}^{\circ} + R \ln \frac{P_0 V}{RT} + \int_{T}^{\infty} \left[\frac{R}{V} - \left(\frac{\partial P}{\partial T} \right)_{V} \right] dV + \int_{T_0}^{T} \frac{C_p}{T} dT . \quad (24a)$$

A similar simplification of (25) yields,

$$H = E_{T_o}^{\circ} + \int_{V}^{\infty} \left[P - T \left(\frac{\partial P}{\partial T} \right)_{V} \right] dV + (PV - RT) + \int_{T_o}^{T} C_{p}^{\circ} dT. \quad (25a)$$

Equation (26) and (27) are obtained by substituting $V = 1/\rho$ and $dV = -d\rho/\rho^2$ into (24a) and (25a) respectively.

$$S = S_{T_o}^{\circ} - R \ln \left(\frac{\rho RT}{P_o} \right) + \int_{0}^{\rho} \left[\frac{R}{\rho} - \frac{1}{\rho} e^{\frac{2\pi}{\sqrt{2T}}} \right] d\rho + \int_{T_o}^{T} \frac{C_p^{\circ}}{T} dT$$
 (26)

$$H = H_{T_o}^{o} + \int_{0}^{\rho} \left[\frac{P}{\rho^2} - \frac{T}{\rho^2} \left(\frac{\partial P}{\partial T} \right)_{\rho} \right] d\rho + \left(\frac{P - \rho RT}{\rho} \right) + \int_{T_o}^{T} C_p^{o} dT \quad (27)$$

It is reemphasized at this point that the necessary low pressure and thus large volume behavior of the real gas equation of state is such that $PV \to RT$. In other words $(\partial P/\partial T)_V$ for the real gas must approach R/V in order to cancel the existing R/V term in (24a). It is clear that if this is not the case, then the remaining R/V term will integrate to ln V which at the upper limit is infinite.

The value of $S_{\mathbf{T}_{\mathbf{C}}}^{\mathbf{C}}$ may be obtained from ideal gas property tabulations. It is noted, however, that $H_{\mathbf{T}_{\mathbf{c}}}^{\mathsf{O}}$ is often tabulated with respect to the ground state energy U_0^0 , i.e., $H_{T_0}^0 - U_0^0$. Thus it is appropriate, if such tables are used, to either tabulate H - $\mathrm{U}_\mathrm{O}^\mathrm{O}$ or assign a value to U_{Ω}^{O} and tabulate H. Frequently it is desired to extend the range of an existing property tabulation, in which case, from an engineering standpoint, it is desirable to choose a reference state on the real gas surface such that the two tabulations agree at that point. The values of $S_{T_0}^O$ and $H_{T_0}^O$ must then be calculated to bring about the desired agreement. The resulting values of $H_{T_{\wedge}}^{O}$ and $S_{T_{\wedge}}^{O}$ are thus based not only on the assigned reference state of the existing tabulation but also on the accuracy with which the equation of state represents the real gas surface. The value of $S_{T_{\mathrm{O}}}^{\mathrm{O}}$ so obtained has no relation whatsoever with the spectroscopically determined ideal gas entropy except when the zero point for entropy has been chosen at 0°K; in this case the agreement of the values of $S_{T_O}^{O}$ determined by the two methods is another check provided by the third law of thermodynamics. The value of $H_{T_0}^{O}$ calculated in this

way is not in conflict with the $H_{T_O}^O$ - U_O^O tabulations based on spectroscopic data since the value of U_O^O is not defined. The value of U_O^O may be arbitrarily assigned thus producing any desired value for $H_{T_O}^O$.

Derivations similar to those above but starting with equations (9a) and (10a) result in equations (26a) and (27a) in which P and T are considered as independent variables.

$$S = S_{T_o}^{o} + R \ln \frac{P_o}{P} + \int_{0}^{P} \left[\frac{R}{P} - \left(\frac{\partial V}{\partial T} \right)_{P} \right] dP + \int_{T_o}^{T} \frac{C_p^{o}}{T} dT$$
 (26a)

$$H = H_{T_o}^{o} + \int_{o}^{P} \left[V - T \left(\frac{\partial V}{\partial T} \right)_{P} \right] dP + \int_{T_o}^{T} C_{p}^{o} dT$$
 (27a)

APPLICATION OF AN EQUATION OF STATE TO THE THERMODYNAMIC EQUATIONS

As an illustration of the application of (26) and (27) the derived properties S and H will be obtained in algebraic form for the equation of state (28) presented by Strobridge [1].

$$P = RT\rho + (Rn_1T + n_2 + n_3/T + n_4/T^2 + n_5/T^4) \rho^2 + (Rn_6T + n_7) \rho^3$$

$$+ n_8T\rho^4 + \rho^3(n_9/T^2 + n_{10}/T^3 + n_{11}/T^4) e^{-n_{16}\rho^2}$$

$$+ \rho^5(n_{12}/T^2 + n_{13}/T^3 + n_{14}/T^4) e^{-n_{16}\rho^2} + n_{15}\rho^6$$
(28)

It will be assumed here that the equations for zero-pressure specific heat, vapor pressure, and the derivative of the vapor pressure with respect to temperature are all available. For example the following forms have been found to be adequate for some fluids.

$$C_{D}^{O} = A_{1} + A_{2}T + A_{3}T^{2} + A_{4}T^{3} + A_{5}T^{4}$$
 (29)

$$\ln P = B_1 + B_2/T + B_3T + B_4 \ln T$$
 (30)

The specific heat integrals may now be replaced by,

$$\Delta S_{P=0} = \int_{T_0}^{T} \frac{c_p^o}{T} dT, \qquad (31)$$

$$\Delta H_{P=0} = \int_{T_0}^{T} C_p^0 dT.$$
 (32)

The derivative $\left(\frac{\partial P}{\partial T}\right)_{\rho}$ with P as defined by (28) is,

$$\frac{\partial P}{\partial T}_{\rho} = R\rho + \rho^{2} \left(Rn_{1} - n_{3}/T^{2} - 2n_{4}/T^{3} - 4n_{5}/T^{5}\right) + \rho^{3}n_{6}R + \rho^{4}n_{8}
+ e^{-n_{16}\rho^{2}} \left[\rho^{3} \left(-2n_{9}/T^{3} - 3n_{10}/T^{4} - 4n_{11}/T^{5}\right) + \rho^{5} \left(-2n_{12}/T^{3} - 3n_{13}/T^{4} - 4n_{14}/T^{5}\right)\right] \cdot$$
(33)

For convenience the following notation is introduced:

$$\int_{\rho_{1}}^{\rho_{2}} - \frac{1}{\rho^{2}} \left(\frac{\partial P}{\partial T} \right)_{\rho} d\rho = S(\rho_{2}) - S(\rho_{1})$$
(34)

$$\int_{\rho_{1}}^{\rho_{2}} \left[\frac{1}{\rho^{2}} \left(\frac{\partial P}{\partial T} \right)_{\rho} - \frac{R}{\rho} \right] d\rho = S'(\rho_{2}) - S'(\rho_{1})$$
 (35)

$$\int_{\rho_{1}}^{\rho_{2}} \left[\frac{P}{\rho^{2}} - \frac{T}{\rho^{2}} \left(\frac{\partial P}{\partial T} \right)_{\rho} \right] d\rho = U(\rho_{2}) - U(\rho_{1})$$
(36)

The quantities $S(\rho)$, $S'(\rho)$ and $U(\rho)$ represent the corresponding indefinite isothermal integrals. These integrals evaluated from (28) and (33) are

$$S(\rho) = -\rho \left(n_1 R - n_3 / T^2 - 2n_4 / T^3 - 4n_5 / T^5 \right) - n_6 R \rho^2 / 2 - n_8 \rho^3 / 3$$

$$- e^{-n_{16} \rho^2} \left(2n_9 / T^3 + 3n_{10} / T^4 + 4n_{11} / T^5 \right) / 2n_{16}$$

$$- e^{-n_{16} \rho^2} \left(\rho^2 / 2n_{16} + 1 / 2n_{16}^2 \right) \left(2n_{12} / T^3 + 3n_{13} / T^4 + 4n_{14} / T^5 \right)$$

$$- R \ln \rho = -R \ln \rho - S'(\rho), \tag{37}$$

$$S'(\rho) = -R \ln \rho - S(\rho)^*, \tag{38}$$

$$U(\rho) = \rho \left(n_2 + 2n_3/T + 3n_4/T^2 + 5n_5/T^4 \right) + n_7 \rho^2 / 2$$

$$- e^{-n_1 6 \rho^2} \left(3n_9/T^2 + 4n_{10}/T^3 + 5n_{11}/T^4 \right) / 2n_{16}$$

$$- e^{-n_1 6 \rho^2} \left(\rho^2 / 2n_{16} + 1 / 2n_{16}^2 \right) \left(3n_{12}/T^2 + 4n_{13}/T^3 + 5n_{14}/T^4 \right)$$

$$+ n_{15} \rho^5 / 5 . \tag{39}$$

Substituting the above relations into (26) and (27) results in

$$S = S_{T_O}^{\circ} - R \ln (\rho RT/P_{\circ}) + \Delta S_{P=O} + S'(\circ) - S'(\rho),$$
 (40)

$$H = H_{T_O}^{O} + U(\rho) - U(0) + P/\rho - RT + \Delta H_{P=O}$$
 (41)

For a point in the liquid region the entropy and enthalpy are given by

$$S = S_{T_{O}}^{O} - R \ln (\rho'''RT/P_{O}) + \Delta S_{P=O} + S'(O) - S'(\rho''')$$

$$- (dP/dT)_{\sigma} (1/\rho''' - 1/\rho'') + S(\rho) - S(\rho''), \qquad (42)$$

$$H = H_{T_{O}}^{O} + U(\rho''') - U(O) + P/\rho''' - RT + \Delta H_{P=O}$$

$$- T(dP/dT)_{\sigma} (1/\rho''' - 1/\rho'') + P/\rho - P/\rho'' + U(\rho) - U(\rho''), \qquad (43)$$

where the Clapeyron relation (20) has been used to cross the two phase region.

^{*} Note that S'(p) exists even at p=0 while S(0) is infinite.

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